

## Magnetite Dissolution Performance of HYBRID-II Decontamination Process

Seon-Byeong Kim\*, Woo-Sung Lee, Hui-Jun Won, Jei-Kwon Moon, Wang-Kyu Choi  
Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, 303-353, Korea  
\*Corresponding author: sbkim@kaeri.re.kr

### 1. Introduction

The decontamination of radioactive isotopes from the primary coolant system of nuclear power plant takes place with the dissolution of oxide layer in which radioisotopes (e.g. Co-60) are deposited inside the layer [1]. The dissolution of metal oxides up to the boundary layer of oxide and base metal is ideally required to remove all radioactivities from the target surface. However, too aggressive solution is deemed to cause the undesirable corrosion damage to the base metal as well as generate a large volume of decontamination waste so that relatively mild decontamination solutions have been developed to date.

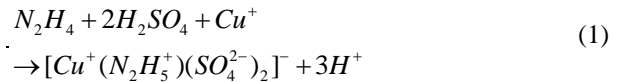
In this study, we conducted the magnetite dissolution performance test of HYBRID-II (Hydrazine Based Reductive metal Ion Decontamination with sulfuric acid) as a part of decontamination process development. Decontamination performance of HYBRID process was successfully tested with the results of the acceptable decontamination factor (DF) in the previous study [2]. While following-up studies such as the decomposition of the post-decontamination HYBRID solution and corrosion compatibility on the substrate metals of the target reactor coolant system have been continued, we also seek for an alternate version of HYBRID process suitable especially for decommissioning. Inspired by the relationship between the radius of reacting ion and the reactivity, we replaced the nitrate ion in HYBRID with bigger sulfate ion to accommodate the dissolution reaction and named HYBRID-II process. As a preliminary step for the decontamination performance, we tested the magnetite dissolution performance of developing HYBRID-II process and compared the results with those of HYBRID process.

### 2. Methods and Results

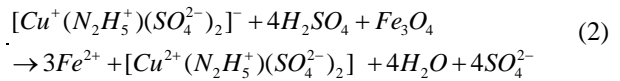
#### 2.1 HYBRID-II Decontamination Process

HYBRID-II decontamination process uses the hydrazine as a strong reducing agent and copper(I) ion as a catalyst to formate a  $[Cu^+(N_2H_5^+)(SO_4^{2-})]^-$  coordination complex in which a hydrazinium ion ( $N_2H_5^+$ ) transfers an electron from a cuprous ion to a ferric ion to be reduced to a ferrous ion. The existence of hydrazinium ion was observed through a single crystal XRD and the complex of nitrogen atom and copper(I) ion was identified by Far-FTIR analysis. The mechanisms of complex formation and decontamination are known as follows.

#### Formation of coordination complex



#### Decontamination



#### 2.2 The Characteristics of Magnetite Dissolution by HYBRID-II Process

As the characteristics of existing processes such as LOMI, CAN-DEREM, or CORD, HYBRID-II (including HYBRID) is a reductive decontamination process as a part of entire multi-step decontamination process in which there is another oxidative process. Strong reductive agent dissolves Fe-rich oxide under acidic environment and the. Therefore we tested the dissolution of magnetite in the form of powder depending on the concentration of reductive agent (i.e. hydrazine) and the strength of acidity. Also, we have the addition of small amount of copper(I) ion since it is reported that the existence of copper(I) ion critically facilitated the dissolution rate of metal oxide [3]. In the test, we got insignificant dissolution rate with 0.001M hydrazine concentration and other results with 0.01M and 0.1M hydrazine concentration as shown in Figure 1.

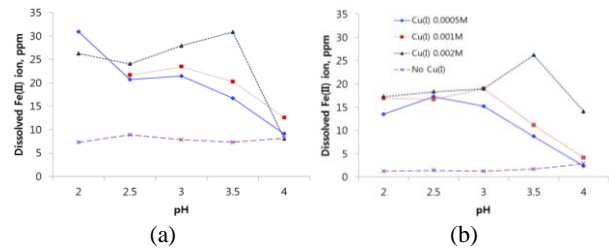


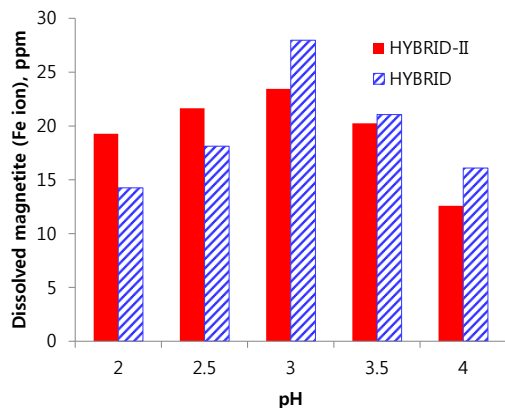
Figure 1. The dissolved magnetite by HYBRID-II decontamination in terms of pH and Cu(I) ion (hydrazine concentration (a) 0.1M, (b) 0.01M)

For both hydrazine concentrations, the highest magnetite dissolution ratio is mostly located in the range of pH 2.5 to 3.5 with the drastic drop-down beyond pH 3.5. The dissolution ratio of the solution without copper(I) ion was much inferior to other solutions containing copper(I) ion. Since a total concentration of magnetite to be dissolved is about 36 ppm in all tests,

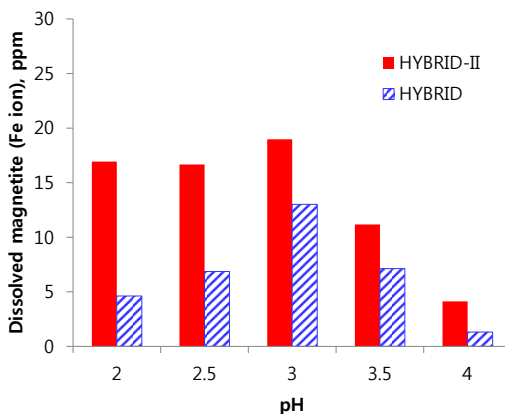
the highest dissolution ratio was about 86% for the solution of 0.1M hydrazine with 0.002M copper(I) ion.

### 2.3 The Comparison of Magnetite Dissolution between HYBRID-II and HYBRID Processes

To acquire the decontamination performance, we compared the magnetite dissolutions by HYBRID-II and HYBRID as shown in Figure 2. The condition of the tests is at 95°C for 2 hours of dissolution with 0.01M and 0.001M hydrazine concentrations and 0.001M copper(I) ion varying the pH in both solutions.



(a)



(b)

Figure 2. The comparison of dissolved magnetite by HYBRID-II and HYBRID processes [conditions: (a) 0.1M N<sub>2</sub>H<sub>4</sub>, 0.001M Cu<sup>+</sup>, 95°C, 2 hours, (b) 0.01 M N<sub>2</sub>H<sub>4</sub>, 0.001M Cu<sup>+</sup>, 95°C, 2 hours]

From this test, we found that magnetite dissolution ratio by HYBRID-II is superior to HYBRID process in the case of 0.01M hydrazine (Figure 2. b) throughout the tested pH range, but selectively superior to HYBRID in the case of 0.1M hydrazine (Figure 2. a). The increased reactivity by sulfate ion in HYBRID-II solution is deemed the factor of higher dissolution ratio of the solution than HYBRID. However, less dissolution ratio of HYBRID-II in some pH range appeared in the former test as Figure 2. (a) might be caused by the precipitation of a certain amount of copper(I) ion by

common ion effect. A close examination to elucidate the reason of this phenomenon will be carried out in the follow-up study of HYBRID-II process.

### 3. Conclusions

HYBRID process developed previously is known have the acceptable decontamination performance, but the relatively larger volume of secondary waste induced by anion exchange resin to treat nitrate ion is the one of the problems related in the development of HYBRID process to be applicable. Therefore we alternatively devised HYBRID-II process using sulfuric acid and tested its dissolution of magnetite in numerous conditions. From the results shown in this study, we can conclude that HYBRID-II process improves the decontamination performance and potentially reduces the volume of secondary waste. Rigorous tests with metal oxide coupons obtained from reactor coolant system will be followed to prove the robustness of HYBRID-II process in the future.

### REFERENCES

- [1] EPRI, Decontamination Handbook, TR-112352, 1999.
- [2] H.J. Won, W.S. Lee, C.H. Jung, S.Y. Park, W.K. Choi, and J.K. Moon. "Dissolution of Fe<sub>3</sub>O<sub>4</sub> by the N<sub>2</sub>H<sub>4</sub> Base Solution", Proc. of The 7th International Conference on Multi-functional Materials and Applications. Huainan, China, 2013
- [3] H.J. Won, W.S. Lee, S.Y. Park, C.h. Jung, W.K. Choi, and J.K. Moon. "Dissolution of Magnetite by the Hydrazine Base Solution", Proc. of Transactions of the Korean Nuclear Society Spring Meeting. 235, Gwangju, Korea, 2013.